

PATENT SPECIFICATION

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(54) COMPOSITE MATERIALS AND MODIFIED FIBRES

(71) We, KJELD HOLBEK, a Danish subject of Lejrevej 74, DK-4320 Lejre, Denmark; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

- 5 This invention relates to composite materials and modified fibres; more particularly, it relates to composite materials comprising certain cellulose-containing fibres which are impregnated, preferably by a vacuum and/or pressure impregnation technique, with at least one wood preservation agent in the fibre structure. Such cellulose-containing fibres and composite materials have novel properties and novel fields of application.
- 10 The present invention provides a composite material which comprises cellulose-containing fibres selected from sulphate pulp fibres, sulphite pulp fibres, semi-chemical pulp fibres, chemi-mechanical pulp fibres, thermo-mechanical pulp fibres and mechanical pulp fibres, or waste paper or waste cardboard fibres or fibre bundles, saw dust, wood chip, shavings, wood wool or synthetic cellulose fibres which are impregnated with at least one agent selected from silicon and metal oxide acylates and biocidally-active metal compounds comprising a metal selected from copper, mercury, chromium, tin and zinc, and a binder.
- The present invention also provides such cellulose-containing fibres which are impregnated with a silicon or metal oxide acylate. Such fibres may be produced by a process which comprises impregnating the cellulose-containing fibres with at least one such agent by 20 a vacuum and/or pressure impregnation technique.
- The impregnation may involve an initial evaporation stage, followed by application of the impregnating agent at normal pressure or at super-atmospheric pressure. The agent may be applied dissolved in a low-boiling organic solvent at a temperature immediately below the boiling point of the solvent. The fibres may be in the form of sheets, rolls or bales which are 25 disbursed immediately subsequent to the impregnation.
- The cellulose-containing fibres, e.g., pulp fibres, such as sulphate pulp fibres, sulphite pulp fibres, semi-chemical pulp fibres, chemi-mechanical pulp fibres, thermo-mechanical pulp fibres and mechanical pulp fibres, for example prepared from soft wood or hard wood, straw or bark. The pulp may be bleached, or unbleached. The pulp fibres may be in the 30 form of, for example, discrete fibres (wet or dry), sheets, rolls, granulates, bales. Important cellulose-containing fibres for the present purposes are waste fibres, for example waste paper or waste cardboard. However, it is also within the scope of the present invention that the cellulose-containing fibres are fibre bundles, saw dust, wood chip, shavings, wood wool or synthetic cellulose fibres. The cellulose-containing fibres are characterized in that they are impregnated with at least one wood preservation agent.
- The impregnation for the production of the fibres may be carried out according to known methods of vacuum and/or pressure impregnation, e.g. impregnation by pressure, in which the impregnating agent is introduced into the material by applying an external pressure, or 35 vacuum impregnation, in which the fibres to be impregnated are first subjected to a vacuum, whereafter the impregnating agent is introduced into the material by releasing the vacuum and optionally applying super-atmospheric pressure. It is also possible to apply alternating pressure-vacuum steps so as to "pump" the impregnating agent through the material.
- Depending upon the solubility characteristics of the impregnating agent, the impregnation 40 may also be performed by using the method wherein impregnation is performed using
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an impregnating agent dissolved in a volatile solvent at a temperature just below the boiling point of the solvent. The solvent may, for example, be methylene chloride, ethylene trichloride, 1,1,1-trichloroethane or fluorotrifluoromethane. Impregnation by this method offers the advantage that the solvent is easily and quickly removed from the impregnated cellulose-containing fibre, thus avoiding the fire hazard of the use of conventional high-boiling fluorinated solvents.

Typical examples of suitable wood preservation agents include: mixtures of copper salts

in carbolinum (anthracene oil), combinations of zinc salts and creosote, salts of mercury,

e.g. mercuric chloride, mixtures of mercuric chloride and copper sulphate with either zinc

chloride or sodium fluoride, fluorine, e.g. mixed solutions of sodium fluoride and zinc

chloride, Wolman salts (generally considered to be formulations containing fluorine,

chromium, arsenic and phenol compounds (FCAP), or fluorine/chromium/arsenic

compounds (FCA), zinc, e.g. basic zinc salts, zinc chloride, chromated zinc chloride

(CZC), copperized CZC (CCZC), copper, e.g. copper compounds, such as copper

sulphate, copper/chromium/boron (CCB) mixtures, copper/chromium/arsenic (CCA)

mixtures, the so-called CCP mixtures wherein the arsenic content of CCA has been

replaced by phosphorous compounds, tin, e.g. triorganotin compounds in emulsified or

solubilized form, such as triphenyltin and tributyltin compounds, such as triethyltin oxide,

tin compounds together with silicon, germylum, lead, (heavy) metal salts, acid

phosphate esters, or metal salts of organic compounds, such as copperpentachlorophenate,

coppernaphthenate, copper-8-hydroxyquinolate, zinc naphthenate or pentachlorophenate,

phosphinate or mercury compounds, such as ethyl mercury chloride, sulphate,

phosphate or acetate or phenol mercury acetate or preferably oleate, or the above-

mentioned organo tin compounds in an organic solvent,

25 One type of compound which has been found especially interesting as an impregnation

agent for use according to the present invention, either alone or in combination with other

wood preservation agents, is the so-called "metal oxide acylates", which a type of

compound invented by Dr. Jacobus Rinse and disclosed, for example, in Belgian Patent

No. 555,969, Netherlands Patent No. 104,261, U.S. Patent Nos. 3,087,949; 3,243,447;

3,177,238; 3,518,287; 3,625,934; 3,546,262; 3,634,674 and 3,673,229 and Belgian Patent

No. 735,548, and U.K. Patent Nos. 1,230,412 and 1,274,718. The metal oxide acylates are

believed to be able to react chemically with the hydroxy groups of cellulose-containing

fibre, resulting in the attachment of a metal acylate group via an oxygen bridge. Metal

oxide acylates may be prepared from a variety of metal oxides, which are capable to provide

35 metal oxide acylates having more than one metal in the molecule. Hence, metal oxide

acylates may be tailored for the present purposes as hydrophobizing agents (aluminum

oxide acylates, such as aluminum oxide fyllate or aluminum oxide stearate or titanium

oxide acylates, such as titanium oxide versate), biocidal metal oxide acylates, such as

40 copper oxide acylates and zinc oxide acylates, and fire-retardant metal oxide acylates, such

as antimony-oxide acylates. Further fastening metal oxide acylates for the present

purposes are oxide acylates of chromium, iron, manganese, and zirconium. Silicon oxide

acylates are also suitable. The oxide acylates are generally soluble in organic solvents and

may be formulated for impregnation accordingly, in conformity with the above-mentioned

methods.

45 The impregnation agents used according to the present invention are preferably so

chosen that they are substantially water-insoluble fixed in the fibre structure, if necessary by

combination with a separate agent improving the fixation. For example, a water-borne salt

impregnation may be combined with a hydrophobization with an effective hydrophobizing

agent, such as aluminum or titanium oxide acylates.

50 The purpose of the present invention is to provide fibres which may be used as

substitution for cellulose fibres in various types of products, and especially, one object of

the present invention is to provide cellulose-containing fibres which may be used as

substitute for asbestos in products conventionally containing asbestos, such as asbestos

60 cement products and brick linings, packings, gaskets seals and washers. However, the

impregnated cellulose-containing fibres may also be used for a wide range of other

applications in which the modified and improved properties thereof are desired.

One of the most important desired properties of the modified cellulose fibres is an

increased dimensional stability, i.e. a minimizing of the tendency of the cellulose-containing

fibres to swell under the influence of water. For many purposes where the cellulose-

containing fibre is to substitute asbestos, it is also desired that it shows a high degree of

65 resistance to deterioration, which means that the cellulose-containing fibres should be

sufficiently impregnated against biodegradation.

An important finding in connection with the present invention is that the impregnation

imparts, to the cellulose-containing fibres, improved properties with respect to the

incorporation thereof in a matrix containing an inorganic binder, such as cement. This is

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believed to be the case especially for impregnation agents which are capable of reducing the inherent capability of the cellulose fibres to attach to each other via hydrogen bonds. If a sheet of the impregnated cellulose fibres is formed, dried and the strength of the sheet determined, the less bonding between the impregnated cellulose fibres in the resulting sheet, the more inert is the impregnated fibre and, it is believed, the more suitable for incorporation in inorganic binder matrices and other purposes where the fibre is to substitute inorganic fibres, such as asbestos.

One advantage of the impregnated fibre is that it may be used as a substitution for asbestos in existing asbestos cement-products such as Hatches and Magnani machines, but the impregnated fibres in the form of pulp fibres may also e.g. be impregnated and web formed on a paper-making machine. Thus, one utility of the cellulose-containing fibres is the application thereof as partially or completely inert fibres in the process described in Belgian Patent No. 861,518, i.e. the fibre may be used to substitute, fully or in part, the mineral fibres used in some of the compositions described. Thus, for example, the fibres impregnated with wood-preserving metal compounds may be used for partial or complete replacement of the mineral fibres in the carpet or flooring backing compositions disclosed in the above. Other composite materials in which mineral fibres may be wholly or partially replaced with the fibres are roofing felt, wall paper, laminated boards, brake linings and other composite materials of the types disclosed in the above, as well as similar composite materials prepared by other methods, including dry methods.

The impregnated fibres may also be used as replacement for glass fibres as reinforcing fibres in composite materials with an organic binder matrix, such as polyester and epoxypolyester. In this case, a web or fleece of the impregnated fibres may be either a dry or a wet method, using a suitable binder, analogously to the preparation of webs or felts produced from glass fibres.

As indicated above, the impregnated cellulose-containing fibres may be produced by a process comprising impregnating the cellulose-containing fibres with at least one of the wood preservation agents by a vacuum and/or pressure impregnation technique. This process may be performed in a manner which is known in connection with wood preservation. The cellulose-containing fibres to be impregnated may be in any desired form, such as granulates, sheets, rolls, bales or, when the fibres to be impregnated are waste fibres, simply in the form of paper waste or cardboard waste. If the impregnation is performed in the same factory where the impregnated fibres are to be used in a wet process, the defibration may be performed immediately subsequent to the impregnation and without any intermediary drying stage. The impregnation technique may also be combined with the preparation of paper pulp, in which case, for example, impregnation with water-borne salts may take place at a stage subsequent to taking up the pulp on the wire, prior to the drying. In this case, the equivalent of a vacuum impregnation treatment may be obtained by pressing the web to a low water content before it passes through the impregnating bath.

Alternatively, impregnation in connection with paper production may, of course, be performed by impregnating a roll of dried pulp in one of the manners described above. The amount of impregnating agent in the impregnated fibres is usually at least 1 percent, by weight, calculated on dry fibre weight, and usually at least 5 percent, by weight, and often from 7 to 10 percent, by weight.

When the fibres are incorporated in a composite material containing cement as binder, the cement content of the composite material will usually be from 25 to 99 percent, by weight, such as from 50 to 90 percent, by weight, and often from 80 to 90 percent, by weight, and the amount of the impregnated cellulose fibers may typically be from 1 to 75 percent, by weight, more typically from 5 to 50 percent, by weight, and often from 10 to 20 percent, by weight, of the composite material. The composite material may, in addition to a cement-binder, contain other inorganic material, such as puzzolan, for example in an amount of from 2 to 20 percent, by weight, calculated on the weight of the cement, fly ash, etc.

Other composite materials with an inorganic binder which may be made using the impregnated fibres are materials in which the binder is a calcium silicate or plaster, and the relative amounts of these inorganic binders and the impregnated fibres may be the same as stated above in connection with cement-bound composite materials.

Composite materials incorporating the impregnated fibres may also contain both an inorganic binder and an organic binder. Especially suitable organic binders for this purpose are polymer materials constituted by solid discreet particles or fibres having polymer at least at the surfaces thereof, the polymer being a water-insoluble solid synthetic polymer which is film-forming on heating, especially such polymer materials which are disclosed in detail in above-mentioned Belgian Patent No. 861,518. The amount of such polymer in composite materials also containing an inorganic binder is usually from 1 to 30 percent, by

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weight, calculated on the total weight of the composite material.

In accordance with what is stated above, a process for preparing a composite material using the impregnated fibres may comprise incorporating the impregnated cellulose fibre material dispersed in water, and when this process is used for preparing a composite material containing an inorganic binder, such as cement, the water retention and flocculation of the system is obtained by using a polyelectrolyte, in accordance with the principles disclosed in the above-mentioned reference. The polyelectrolyte is preferably of the neutral or anionic type. Accordingly, one aspect of the present invention relates to a composite material comprising the impregnated cellulose-containing fibres and additionally comprising a polyelectrolyte. A polyelectrolyte may also be a useful flocculation agent in the composite materials which use an organic binder, *vide* the disclosure of the above-mentioned reference.

When a polymer which is film-forming on heating is incorporated in the composite material also incorporating an inorganic binder, a suitable method of preparing such composite material comprises subjecting the resulting material, after the shaping to the desired configuration, to a treatment eliciting the film-forming properties of the polymer. The treatment eliciting the film-forming properties of the polymer may be performed after the curing of the inorganic binder, or the treatment eliciting the film-forming properties of the polymer may be performed prior to curing of the inorganic binder, and, subsequently to the eliciting of the film-forming properties of the polymer, the amount of water necessary for curing the inorganic binder may be added, wherever the film-forming may be performed. Another possibility is to combine curing of the inorganic binder and eliciting of the film-forming properties of the polymer in one treatment, for example in autoclave, depending upon the particular binder and polymer used.

When composite materials using the impregnated fibres and with an inorganic binder are produced by a wet method, another possibility for obtaining improved dispersion of the impregnated fibres is to use an oil as dispersing aid, possibly combined with the use of a polyelectrolyte. The oil may suitably be a non-drying oil which may be added to the fibres in the form of an emulsion.

The impregnated cellulose-containing fibre materials may be defibrillated by conventional methods, for example wet defibrillation in a pulper, or dry defibration.

In the present context, the term "hydrophobizing agent" is intended to designate not only agents which impart true hydrophobicity to the treated fibres, but also agents which change the properties of the fibres in direction from hydrophilicity towards hydrophobicity.

In the present context, the term "cement" is intended to designate both portland cement types and the other inorganic cement types.

EXAMPLE 1

Unbleached sulphate cellulose fibres in sheet form were impregnated with a CCA agent composition: arsenic, chromium and copper compounds in quantitative ratios corresponding to As_2O_5 : 34.0% \pm 2%, Cr_2O_3 : 26.6% \pm 1.5%, CuO : 14.8% \pm 1%, H_2O : 26.5% \pm 4% in two different ways:

I. The specimen was evacuated to about 60 mm Hg with a water jet air pump and was left for 20 minutes in the impregnating liquid, whereafter the pressure was raised to atmospheric pressure and the specimen was left for a further 20 minutes.

II. The specimen was evacuated to approximately 60 mm Hg, and the pressure was again raised to atmospheric pressure. This cycle was repeated 20 times within 20 minutes, whereafter the specimen was left for a further 20 minutes at atmospheric pressure in the impregnating liquid.

The water content of the fibres impregnated according to method I or II was determined by weighing during drying until constant weight at 105°C.

The copper, chromium and arsenic contents were determined in the dried specimens. A known quantity of impregnated fibres of specimens I and II were beaten, that is dispersed in water, by means of a blender. Specimens were taken out for washing out experiments. Washing out experiments were performed on the beaten fibres impregnated according to method I or II by the following two methods:

A. Washing with hot water (30°C) for 2 hours under simple stirring with a propeller, the fibre concentration being approximately 2 g/litre water.

- B. Washing at 20°C for 24 hours with a calcium hydroxide solution at pH 12.0 under simple stirring with a propeller, the fibre concentration being approximately 10 g/litre solution.
- 5 After the washing experiments, copper, chromium and arsenic contents were determined in both the washing liquids and the washed fibres. The water contents in specimens I and II and the results of weighing of fibres are listed in Table I below.
- 10 The results of the determinations of the copper, chromium and arsenic contents are listed in Table II below. The figures are in mg metal per g dry fibre used.

TABLE I.

	<i>Fibres impregnated according to</i>	<i>Method I</i>	<i>Method II</i>	
15	Water content in fibres	57.1%	58.9%	15
20	Beating of specimens (moist) in water	100 g in 200 ml	50 g in 500 ml	20

In diluting the beaten specimens for the washings, there was corrected for the initial water content of the specimens, and hence, the below-listed concentrations of fibres in 25 washing liquid represent dry fibres.

Fibre concentration in the washing experiment.

30	Washing A	2.21 g/1000 ml	2.12 g/1000 ml	30
	Washing B	5.36 g/500 ml	5.14 g/500 ml	

TABLE II.
Content of Copper, Chromium and Arsenic in the Fibres

<i>Method of impregnation</i>	<i>Copper</i>		<i>Chromium</i>		<i>Arsenic</i>	
	I	II	I	II	I	II
Content in mg/g in unwashed, impregnated fibres	13.41	13.17	13.6	15.57	16.50	16.81
	{ 13.75	{ 13.15	{ 13.2	{ 16.33	{ 15.3	{ 26.12
					{ 15.72	{ 26.26
						26.4
Washed out according to method A, %	24	13	41	25	29	25
Content in fibres, determined after washing, according to method A, %	76	87	59	75	71	75
Washed out according to method B, %	0.8	1.4	33	23	4	5
Content in fibres, determined after washing, according to method B, %	99.2	98.6	67	77	96	95

The determination of the copper, chromium and arsenic contents in the fibres shows that the fibres were impregnated equally according to the two methods, and that there were the same proportions of copper, chromium and arsenic in the fibres as in the corresponding liquid. The total impregnation corresponds to an uptake of salts of from 8 to 9% of the weight of the fibres.

In the washing experiments with water according to method A, part of the copper, chromium and arsenic contents in the fibres was washed out, mostly from the fibres impregnated according to method I.

In the washing experiments with calcium hydroxide solution according to method B, practically no copper and little arsenic were washed out, while approximately as much chromium was washed out as in the washing experiment A. As regards chromium, again most was washed out from the fibres which were impregnated according to method I. As regards copper and arsenic, the difference in washing out from the fibres impregnated according to method I or II was so little that it was within the uncertainty of the method.

Sheets of sulphate cellulose fibres impregnated with a CCA agent as above in the manner described above were defibrated in water to yield 1/2% suspension. The defibration required about 50% more beating time than the defibration of corresponding untreated sheets. After the defibration, the suspension was converted into sheets on a laboratory sheet former and dried in an oven at 100°C. After the drying, the resulting sheets showed much less strength than corresponding sheets made from untreated starting fibres: the fibres of the sheets made from the impregnated material could easily be drawn from each other and showed virtually no coherency except that resulting from the entangling.

EXAMPLE 2.

Scanning Electron Microscopy (SEM) on Impregnated Fibres.

Various sorts of fibres were impregnated with various impregnation agents according to various methods, as stated in the below scheme, whereafter SEM was performed on the fibres and the contents of S, Ca, Cr, Cu and As were determined by X-ray analysis.

The determinations show that there is no significant difference between the degree of impregnation at the middle of the fibre, at the surface or in between, which indicates that the impregnating agent penetrates into and is evenly distributed in the cell and not only impregnates the surface.

Experiments 6 and 7 show the effect of pressure impregnation. Experiments 4 and 6 show that the impregnation is improved if the specimen is evacuated before the pressure influence, and the experiments 1 and 4 indicate that the impregnation is improved to a higher extent by application of longer acting evacuation than by application of a higher pressure after the evacuation.

Fibre	Impregnating agent	Impregnating process					
		S	Ca	Cr	Cu	As	
1. Unbleached sulphate	CCA agent (0.6%)	Vacuum (60 mm Hg) for 20 minutes - atm. pressure in between 15 minutes - 10 kg/cm ² for 20 minutes	middle in between surface	256 345 446	1480 426 443	850 916 1722	466 598 612
2. Semichemical beach cellulose	CCA agent (0.6%)	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm ² for 60 minutes	middle in between surface	812 736 736	181 244 194	589 633 630	216 230 234
3. Unbleached sulphate	Goni 22 "green kobber"**	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm ² for 60 minutes	middle in between surface	692 623 553	631 695 581	0 0 0	820 2632 3210
4. Unbleached sulphate	CCA agent (0.6%) + 1% Malogenen** El 719	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm ² for 60 minutes	middle in between surface	183 157 193	307 348 396	278 304 380	110 170 136
5. Corrugated paper	CCA agent (0.6%) + 1% Malogenen** El 719	Vacuum (60 mm Hg) for 15 minutes - 10 kg/cm ² for 60 minutes	middle in between surface	111 99 92	114 140 124	938 947 876	238 278 240
6. Unbleached sulphate	CCA agent (0.6%) + 1% Malogenen** El 719	Submersed for 20 minutes	middle in between surface	116 102 92	288 388 333	78 78 106	44 62 130
6a. Unbleached sulphate	CCA agent (0.6%) + 1% Malogenen** El 719	Submersed for 20 minutes	middle in between surface	150 163 193	331 346 349	283 297 283	100 98 96
7. Unbleached sulphate	None	Not treated	middle in between surface	247 200 260	347 424 428	0 8 11	0 14 0

* (25% solution of copper naphthalene in white spirit)

** (Malogenen is a trade mark; emulsifier based on polyethoxylated alcohols)

EXAMPLE 3.

Strips of filter material made of bleached sulphate cellulose were dipped for one second in a solution of 7 parts, by weight, of Frigen (Registered Trade Mark) S11 (fluorotrichloroethylene) and 1 part, by weight, of metal oxide acylate containing 30% of white spirit. The strips were dried in an oven at 100°C for one hour. The metal oxide acylates used were titanium oxide stearate (D-14-00), zinc oxide versate (E-12-80, containing only 20% of white spirit), aluminium oxide phthalate (C-10-70), aluminium oxide stearate (C-14-70) and aluminium oxide stearate/phthalate (C-10/14-70), all supplied by MOACO S.A., Echallens, Switzerland. The impregnated paper strips, with the exception of the strips treated with zinc oxide versate, showed hydrophobicity, especially the specimen impregnated with titanium oxide stearate, and all the impregnated paper strips, including the zinc oxide versate-treated strip, showed less elongation upon dipping in water than the controls.

- 5 The strips were defibrated by beating in water in a blender. The zinc oxide versate-treated strip was defibrated as easily as the untreated strips, while about 5% longer treating time was required for the defibration of the other metal oxide acylate-treated strips. After the defibration, the pulp of aluminium oxide phthalate-treated fibres was converted into a sheet in a laboratory sheet former, and the sheet was dried in an oven at 100°C for one hour. The resulting dried sheet showed considerably less strength than a corresponding sheet made of untreated fibres, indicating little or no chemical bonding between the fibres.

- 10 **EXAMPLE 4.**
The sheet of the CCA agent impregnated fibres made in a laboratory sheet former and thereafter dried (*vide* Example 1) was dipped into a solution of 1 part of titanium oxide stearate (D-14-00 from MOACO S.A.) in 7 parts of Frigen S11 for one second. Thereafter, 15 the fibrous mass was dried in an oven at 100°C for one hour. After the drying, the material showed excellent hydrophobic properties, in contrast to the CCA agent impregnated fibres which had not been treated with titanium oxide stearate.

- 20 **EXAMPLE 5.**
Sulphate cellulose pulp was impregnated with the CCA agent as described in Example 1, by method I. The impregnated fibre had a salt content of 5%, by weight. The resulting impregnated sheet of fibre pulp was defibrated in a blender and, to the defibrated sheet, dry cement consisting of 40 g of dry material consisting of impregnated fibres was added 160 g of cement (super rapid). The quantity of water present was such that the total content of dry matter, cement + fibres, was approximately 1/2%, by weight. The suspension was poured into the chest of a sheet-former, and immediately before the water was suctioned off, a polyelectrolyte was added in a quantity of 0.04%, calculated on the dry matter. The polyelectrolyte was in one run Prodefloc C1 and in another Prodefloc N2M. By 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 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EXAMPLE 8.

The process described in Example 5 was followed, but additionally, 5%, by weight, of epoxypolyester powder, calculated on the total dry matter, was added together with the cement. After one day of curing in a plastic bag, the board was removed and placed for 5 drying at 100°C in an oven, and when the board had dried to constant weight, the temperature was raised to 200°C, and the board was kept for 2 minutes at 200°C. After cooling, the board was moistened again so that the cement could continue curing. After curing, the board had an excellent tensile strength and a tight, smooth and beautiful surface. A similar experiment was performed using a smaller amount of water, *viz.* a water/cement ratio of approximately 50. A similar excellent result was obtained.

EXAMPLE 9.

Sulphate cellulose pulp was impregnated with the CCA agent as described in Example 1, method I. The impregnated fibres had a salt content of 5%, by weight. The resulting impregnated sheets of fibre pulp were delibrated in a blender and the delibrated suspension in a quantity corresponding to 8.5 g of dry material consisting of impregnated fibres was admixed with 66.5 g of cement (rapid), 30 g of amorphous silica (TMS) and from the production of ferrosilicon) and 5 g of a powder epoxypolyester (55% by weight applied on 43%, by weight of TiO_2) and 5 g of $NaSO_4$ particle size from 30 to 80 μ . Water was added until the total content of dry matter in the resulting suspension was about 4%. The suspension was poured into the chest of a laboratory sheet former, and immediately prior to suctioning off the water, 0.5 of Prodefflo N2M (a polyelectrolyte) was added. By suctioning off the water, a sheet was formed which was allowed to cure for about 12 hours. Thereafter, the sheet was kept for about 1 hour in an oven at 100°C and subsequently for about 15 minutes at 220°C. The resulting board had a smooth surface and showed uniform fibre distribution.

WHAT WE CLAIM IS:-

1. A composite material which comprises cellulose-containing fibres selected from sulphate pulp fibres, sulphite pulp fibres, semi-chemical pulp fibres, chemi-mechanical pulp fibres, thermo-mechanical pulp fibres and mechanical pulp fibres, or waste paper or waste cardboard fibres, or fibre bundles, saw dust, wood chip, wood wool or synthetic cellulose fibres, which are impregnated with at least one agent selected from silicon and metal and oxide acylates biocidally-active metal compounds comprising a metal selected from copper, mercury, boron, arsenic and zinc, a binder and a hydrophobizing metal oxide acylate.
2. A composite material as claimed in claim 1 wherein the fibres are in the form of discrete fibres in dry or wet state or in the form of sheets, rolls, bales or granulates.
3. A composite material as claimed in claim 1 or claim 2 wherein fibre bundles, saw dust, wood chip, wood wool, or synthetic cellulose fibres are used.
4. A composite material as claimed in any of claims 1 to 3 wherein the agent is selected from copper naphthenate, CCA agents, CCP agents and other copper-chromium impregnation agents.
5. A composite material as claimed in any of claims 1 to 4 wherein the metal oxide acylate is a hydrophobizing metal oxide acylate.
6. A composite material as claimed in claim 5 wherein the hydrophobizing metal oxide acylate is an aluminium oxide acylate or a titanium oxide acylate.
7. A composite material as claimed in any of claims 1 to 4 wherein the metal oxide acylate is a biocidally-active metal oxide acylate.
8. A composite material as claimed in claim 7 wherein the biocidally-active metal oxide acylate is a zinc oxide acylate.
9. A composite material as claimed in any of claims 1 to 8 wherein the fibres are impregnated with both a biocidally-active metal compound and a hydrophobizing and/or flame-retarding metal oxide acylate.
10. A composite material as claimed in any of claims 1 to 9 wherein the binder is an organic polymer.
11. A composite material as claimed in any of claims 1 to 9 wherein the binder is an inorganic binder.
12. A composite material as claimed in any of claims 1 to 9 wherein the binder is a combination of an inorganic and an organic binder.
13. A composite material as claimed in any of claims 1 to 12 containing a polyelectrolyte.
14. A composite material as claimed in claim 1 substantially as herein described.
15. A process for the production of a composite material as claimed in claim 1 substantially as herein described.

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16. Cellulose-containing materials as defined in claim 1 which are impregnated with a
silicon or metal oxide acylate.
17. A process for the production of materials as claimed in claim 16 substantially as
herein described.

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